

Salinity Measurements and Use of the Practical Salinity Scale (PSS)

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Abstract

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Salinity, temperature and pressure are parameters which govern the oceanographic state of a marine water body and together they make up density of seawater. In this contribution we will focus our interest on one of these parameters, the salinity: accuracy in relation to different purposes as well as observation technique and instrumentation. We will also discuss the definition of salinity. For example most of the Indian Ocean waters are within the salinity range from 34.60 - 34.80, which emphasize the importance of careful observations and clear definitions of salinity, in such a way that it is possible to define water masses and predict their movements. In coastal waters the salinity usually features much larger variation in time and space and thus less accuracy is sometimes needed.

Salinity has been measured and defined in several ways over the past century. While early measurements were based on the amount of salt in a sea water sample, today the salinity of seawater is most often determined from its conductivity. As conductivity is a function of salinity and temperature, determination involves also measurement of the density of seawater is now more precisely estimated and thus the temperature. As a result of this method the Practical Salinity Scale (PSS) was developed. The best determination of salinity from conductivity and the temperature measurements gives salinity with resolution of 0.001 psu, while the accuracy of titration method was about $\pm 0.02 \text{ ‰}$. Because of that, even calculation of movements in the ocean are also improved.

Introduction

Spatial distribution of salinity and temperature provide oceanographers with information that enables them to trace the circulation patterns of the ocean. The state of seawater depends on three quantities, absolute temperature (T) thermodynamic pressure (p) and sea salinity (S). The relation between the density (ρ) and the three basic thermodynamic variables is called the equation of state $\rho = \rho(S, T, p)$. Whereas the absolute sea level is an indication of surface movements, density of the water indicates the dynamics of the interior ocean. Even small horizontal differences, thus in density and pressure may cause strong currents.

The density of seawater is rarely measured by itself, but normally calculated from measurements of temperature, conductivity or salinity and pressure using the equation of state. This equation involves several coefficients describing the relationship between the individual parameters (Gill, 1982). In the surface waters of the oceans, however temperature and salinity alone determines the density of water and the equation of

state is reduced to $\rho = \rho_0(1 + \alpha T + \beta S)$; where $\alpha = -\frac{1}{\rho} \frac{d\rho}{dT}$ and

$\beta = +\frac{1}{\rho} \frac{d\rho}{dS}$ The density decreases (contraction) with the decreasing

salinity. Neither α nor β are general constants but $\beta \approx 0.8 \times 10^{-3}$, almost independent of temperature, whereas α varies considerably with temperature. If the salinity value is above 24.7 psu, decreasing temperature causes an increase of density (expansion). For lower salinities, the density at first increases and reaches maximum between -1.33 and $+3.98$ $^{\circ}\text{C}$ depending on the salinity value, and then decreases down to the freezing point (Gill, 1982). This means that α varies from -0 to 0.3×10^{-3} . For tropical temperatures ($20 - 30^{\circ}\text{C}$) and salinities of around 35, however, $\alpha \approx 0.2 - 0.3 \times 10^{-3}$

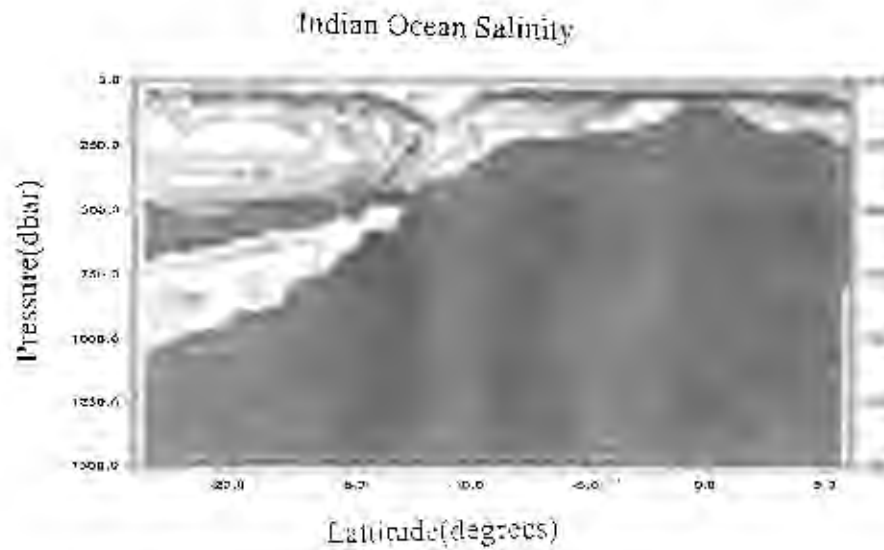
Constancy of the composition of seawater was first recognized by Forchhammer (1865), who noted that even though the total salt content of sea water samples varied, the ratio of the major dissolved components were essentially constant. It was further confirmed by Dittmar (1884), who analyzed seawater for the elements chlorine, sodium, magnesium, sulphur, calcium, potassium and bromine from samples collected at various depths. The analysis was based on the samples from Challenger

Expedition (1872-86). Dittmar suggested that determination of the quantity of a single major component in seawater (i.e. chlorine) could be used to determine the salinity of a seawater sample. Encouraged by the International Council for the Exploration of the Sea (ICES), Kundsén et al. (1902) developed a volumetric method for the determination of the chloride content and thus of salinity (see further below). They created a consistent set of algorithms for computing various properties (potential temperature, density etc) from the basic observations of chlorinity, temperature and depth.

In 1960, the British National Institute of Oceanography (NIO) studied a wide range of seawater samples, and reported markedly higher correlation between density and conductivity than between density and chlorinity. Thus the Joint Panel On Oceanographic Tables And Standards (JPOTS) meeting in 1964 casted doubts about the principal of constancy of composition and on the precision of salinity measurements based on chlorinity. JPOTS concluded that density could be estimated more precisely from conductivity than from chlorinity. With the availability of accurate conductivity sensors in the early 1970's, the JPOTS adopted (Unesco Report No. 38, 1981) the Practical Salinity Scale (PSS-78) and the International Equation of State for Seawater (EOS80). According to this, salinity is defined from conductivity, breaking the link with chlorinity. Thus, defining the practical salinity in terms of the ratio K_{15} of the electrical conductivity of the seawater sample at the temperature of 15 °C and the pressure of one standard atmosphere, to that of potassium chloride (KCl) solution, in which the mass fraction of KCl is $32.4356 \cdot 10^{-3}$ at the same temperature and pressure.

Salinity determination from Conductivity

Sea salt is an electrolyte mixture which is completely dissociated in water into its component ions. Each ion carries an electric-charge and is free to move. Every ion contributes to the electrical conductance of the sea water solution. More salt increases the conductivity, almost (though not exactly) in direct proportion. Oceanographic sensors cannot measure conductivity directly; instead they measure conductance, i.e. the voltage produced in response to the flow of a known electrical current.



Source: National Oceanic & Atmospheric Administration, USA

Fig.1: Salinity profile along the longitude 80° E from R/V Knorr- Mar. 1995

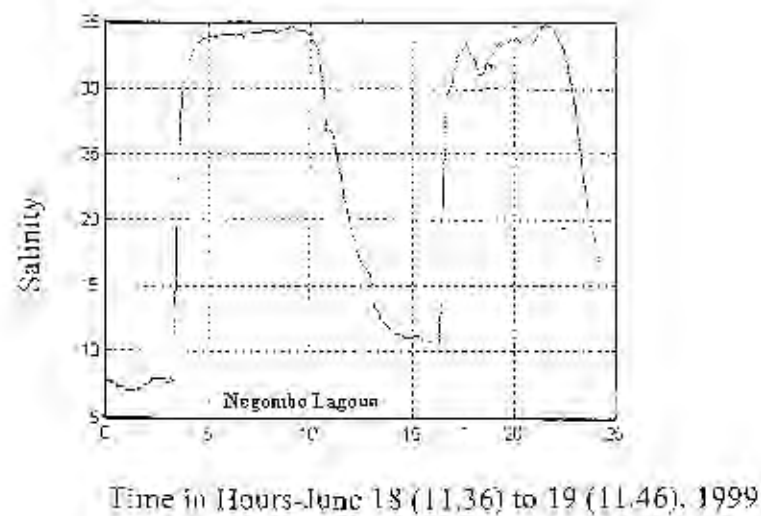
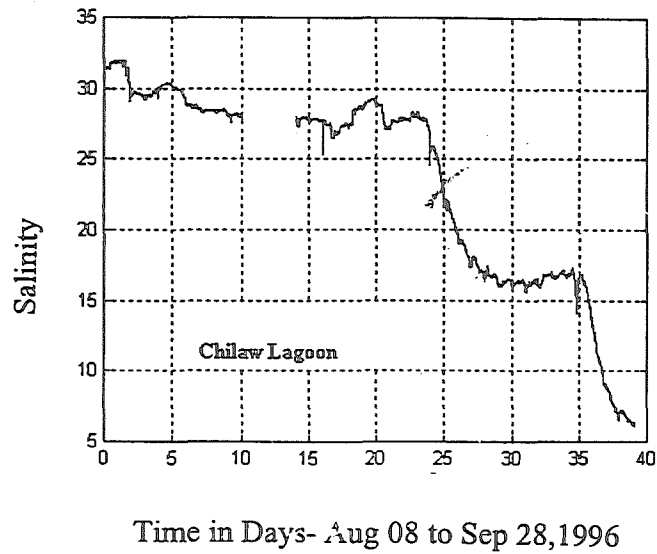
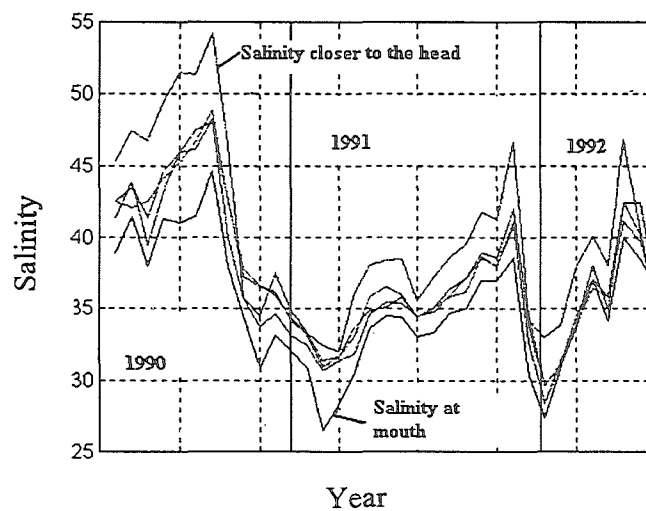


Fig.2: Tidally induced Salinity Fluctuation



**Fig.3: Freshwater discharge induced salinity fluctuation
(Monthly)**



**Fig.4: Section-wise vertically averaged salinity
-Puttlam Lagoon (Yearly)**

Conductivity is calculated from the conductance measured by the sensor using a cell constant (C), which reflects the ratio of length and cross sectional area of the sampled water volume in which the electrical current actually flows.

Determination of conductivity is carried out from the relationship

$R = \frac{\rho L}{A}$; where R = resistance = conductance⁻¹, ρ = resistivity = conductivity⁻¹, L = Length of sampled water volume and A = cross-sectional area of the sampled water volume. In order to obtain high accuracy with a laboratory salinometer (e.g. AutoSal), the electrical conductivity of aqueous solutions is obtained by measuring the resistance between two platinum electrodes immersed in the solution. The specific conductivity (κ) is calculated directly from the measured resistance (R)

and the cell constant (C) by $\kappa = \frac{C}{R} \text{ ohm}^{-1} \text{ cm}^{-1}$. As mentioned, the cell constant is the ratio of the length to cross-sectional area of the electrical path, and its value is usually established by calibrating the conductivity cell with a standard solution of well known conductance. In addition the cell is submerged in ambient water of similar temperature as that of the sample, which means that sea water samples must be stored for some hours in laboratory before being analysed.

Attempts were made to build *in-situ* salinometers (Figs. 7-8) including a temperature compensating system, according to the same principles as those for the laboratory salinometers. But a slightest deformation of the electrodes by mechanical shock, corrosion or fouling by organisms appreciably changes the cell constant. To overcome with these difficulties, ingenious induction salinometers such as CTD's (STD), Bathysondes, and Multisondes, where electrodes are not directly exposed to seawater were devised. Sensors for temperature and pressure observations were measuring simultaneously thus enabling the instrument to be used for salinity measurement in the deep oceans.

(Fig.7) or may transmit the data by a cable or single conductor armoured wire up to a surface deck unit, which is a micro-processor or numeric display unit (Fig. 8). Laboratory instruments are capable of analysing discrete water samples stored in a dark brown bottles (Fig. 6). Self contained instruments for logging internally (on e.g. current meter) or for a surface based logging unit via cable also available (Fig. 5).

Accuracy of the conductivity based instruments differs considerably depending on design of electrical connection to the seawater (electrodes or transformers), but also on the maintenance of the cell geometry, which provide the cell constant for the salinity determination from conductivity. Accuracy of most of the instruments range from 0.01 to 0.001 psu. Less resolution (~1 psu) is common on instruments for long term logging of salinity. It is not uncommon that such instruments feature a drift due to cell contamination (Bryden et al., 1994).

Conductivity based field salinometers are either self contained (internally) recording instruments

Other methods for salinity determinations

Gravimetric determination

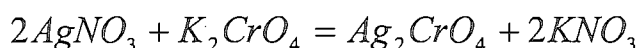
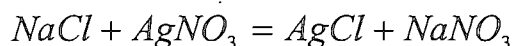
The salinity of a sea water sample can be measured by evaporating the water and weighing the solid residue - the salt. This is called gravimetric determination. Unfortunately, salt retains variable amounts of H_2O molecules, so this weight measure is not precise. Marine chemists in the 19th century were well aware of this disadvantage in their attempts to measure salinity gravimetrically, and devised procedures that gave reasonably reproducible results.

Chlorinity titration

The principle of “constant proportion” presumes that the quantity of one single major ion is enough to specify the salinity of water. Chemists, for a variety of logical reasons, chose Cl^- as indicator of salinity. Specific salinity index involves the determination of not just of Cl^- but of chlorinity, or the total amount of halogens dissolved in water expressed in g/kg. The members of halogen family which includes chlorine, bromine, iodine and fluorine, are difficult to distinguish analytically because of their common chemical properties. The accuracy required for titration is obtained by using a special type of glass apparatus – a Knudsen burette and a Knudsen pipette.

A Knudsen burette is filled with a solution of silver nitrate. The seawater sample is put with a Knudsen pipette into a beaker, and a bit of potassium chromate solution is added. While stirring, the silver nitrate solution runs as a thin stream into the yellow-coloured seawater sample, whereupon silver chloride precipitates in the seawater sample forming a white gaseous deposit. When all the chlorine ions that were contained in the

seawater sample have precipitated as silver chloride, silver chromate is formed (red colour appears on the deposit). From the amount of silver nitrate needed up to the point where the change of colour takes place, and from the amount of seawater used, the chloride content of the seawater sample can be calculated. Chloride titration according to Mohr is based on the following chemical formulas (see Dietrich et al., 1980):



The salinity is calculated from the formulae; $S = 0.030 + 1.8050 \text{ Cl}$

Here S is the salinity in ‰, the total weight of salt in 1000 grams of seawater. Cl is the amount of chlorine in ‰, the weight of chlorine in per 1000 grams of seawater (Knudsen, 1959). An accuracy of ± 0.02 ‰ in the determination of salinity is attained by comparative measurements with a standard water sample.

Methods based on density or refractive index measurements

Instruments using the density or refractive index observation should be employed only when demands on accuracy and applicability are low.

So called density areometers are used in the form of calibrated glass floats, mostly stalk areometers; the water sample is filled into a cylinder, care is taken that the temperature is balanced, and the areometer is put in. From a calibrated scale (graded in ‰ salinity) in the stalk of the areometer, the distance that the instrument is immersed in the seawater can be read. Simultaneous measurement of temperature are necessary to obtain the salinity. This method is simple but yields accuracy of about $\Delta S = \pm 0.1$ ‰ only.

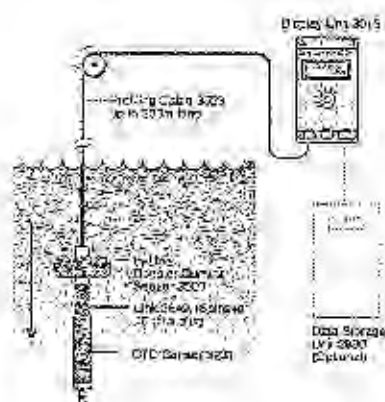


Fig.5: Cabled self recording salinometer for long term in-situ recording

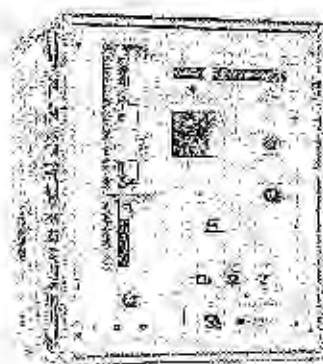


Fig.6: Laboratory salinometer for analysis of water sample



Fig.7: Self contained salinometer (no cable)extra equipped - for battery forcing and readout after deployment

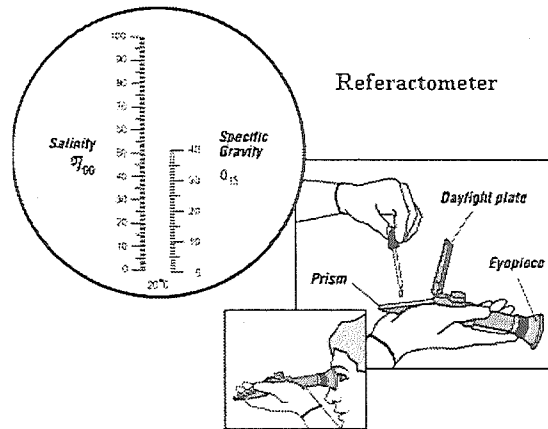


Fig.8: Cabled salinometer for vertical profiling with display for direct readout

The refractive index increases with salinity by about 2×10^{-4} per psu and with temperature by about 0.1×10^{-4} per $^{\circ}\text{C}$. According to Rusby (1967), the salinity is obtained from difference $\Delta\eta$ between the refractive index $\eta_{s,T}$ of a seawater sample and the refractive index $\eta_{35,T}$ of standard seawater with 35.00 psu salinity at the temperature T and atmospheric pressure as follows.

$$S = 35.00 + 5.3302 \times 10^{-3} \Delta\eta + 2.274 \times 10^5 \Delta\eta^2 + 3.9 \times 10^6 \Delta\eta^3 \\ + 10.59 \Delta\eta(T - 20) + 2.5 \times 10^2 \Delta\eta^2(T - 20)$$

This equation holds for the ranges of $30.9 \leq S \leq 38.8$ and $17^{\circ}\text{C} \leq T \leq 30^{\circ}\text{C}$ for the light of the green Hg line at a wavelength of $\lambda = 546.227 \text{ nm}$. The refractive index decreases by about 4% at an increase of the wavelength from 250 to 1250nm. Refractometers show better accuracy ($\pm 2 \text{ psu}$) on the water with the salinity of 20 – 40 psu and becomes less accurate



**Fig.9: Refractometer-not expensive, simple to use,
limited accuracy & applicability**

beyond the range. Arulanathan et al. (1995) calibrated refractometer observations against the laboratory determinations with laboratory salinometers (AutoSal) and obtained the relation $S_a = 0.8249S_r + 5.358$; where S_a = AutoSal salinity and S_r = Refractometer salinity.

Sampling technique

Salinity measurements are used by oceanographers and marine biologist for different purposes, and may require different precision. Studies of transport and flushing in estuaries require less precision (~ 0.1 psu) than studies in the deep ocean (~ 0.01 psu or better). For ecological studies, on the other hand, a precision of 1 psu may be satisfactory. Tracing different water masses in an estuary and saltwater intrusion upstream in a tidal regime requires repetitive sampling at the same location, at least over a tidal cycle but also over a longer period (months), because of varying discharge and climate (evaporation, heating, cooling, wind, etc.) such cases may comprise different accuracy. In general, coastal waters needs more narrow spaced sampling than open ocean studies. For instance, in the open ocean a spacing of 50 to 100 km may be adequate but at the coastal water bodies it may be necessary to reduce this to between 1 - 10 km or even less. Seasonal variations in climate is a reason for large scale variations in the coastal water bodies. In order to obtain a complete picture of oceanographic conditions, it might therefore be necessary to extend observations over one full year or more. A number of oceanographic cruises covering different seasons are necessary.

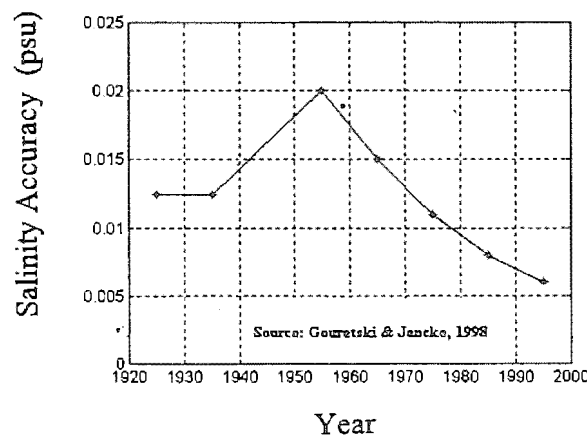


Fig.10: Sampled at depths below 1500 m in the South Atlantic from 1920 to 1993.

Conclusions

During the last century, the salinity has been measured by several different methods, although chlorinity titration and conductivity were most common. Highest accuracy is reached from conductivity measurement followed by titration methods (Fig. 10).

Density and refractive index may also be used to determine salinity, though they do not meet the international standards of accuracy. Development of CTD (conductivity, temperature and depth) instruments for salinity determination in the 20th century simplified both the coastal and deep ocean observations giving a precision of better than 0.01 psu. A variety of both self-contained instruments (with internal data logger) and onboard direct reading instruments are available at prices between 5,000-50,000 US\$.

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